

Review article

Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents

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Abstract

Advanced oxidation processes (AOPs) constitute a promising technology for the treatment of wastewaters containing pharmaceuticals and personal care products (PPCPs) and especially endocrine disrupting chemicals (EDCs). Data concerning the degradation of PPCPs and EDCs by means of AOPs reported during the period January 2000–May 2007 are evaluated in this work. Ozonation was the oxidation process most studied, gives the best expectatives to be applied with successful results.

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1. Introduction

The contamination of water by refractory organic substances significantly affects the viability of water reuse of treated municipal or industrial water effluents. Historically, compounds as substituted phenols, non-biodegradable chlorinated solvents, pesticides and surfactants are recognized as examples for relevant substances difficult to remove from water. Recently, pharmaceuticals and personal care products (PPCPs) and

especially endocrine disrupting chemicals (EDCs) are considered as emerging contaminants, which means that they are still unregulated or in process of regularization [1]. EDCs and PPCPs are emerging environmental contaminants that in very small concentrations may cause disruption of endocrine systems and affect the hormonal control of development in aquatic organisms and wildlife [2].

EDC have been defined by the Organization of Economic and Cooperative Development (OECD) as “an exogenous substance or mixture that alters the function(s) of the endocrine systems and consequently causes adverse health effects in an intact organism, or its progeny or (sub) populations” [3]. A wide range of chemical compounds have been found to be capable of disrupting the endocrine systems. As shown in Table 1,

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Nomenclature

AOPs	advanced oxidation processes
CEC	commission of the European Communities
COD	chemical oxygen demand
CSTEE	Committee on Toxicity, Ecotoxicity and the Environment
$C_{\text{Fe}^{2+}}$	iron concentration
$C_{\text{H}_2\text{O}_2}$	hydrogen peroxide concentration
C_{O_3}	ozone concentration in gas phase (unless indicated)
C_{TiO_2}	titanium dioxide concentration
C_0	contaminant concentration
DDE	2,2-bis- <i>p</i> -chlorophenyl-1,1-dichloroethylene
DDT	2,2-bis- <i>p</i> -chlorophenyl-1,1,1-trichloroethane
DOC	dissolved organic carbon
DWTP	domestic wastewater treatment plant
EDCs	endocrine disrupting chemicals
EPA	Environmental Protection Agency
EU	European Union
I	radiation flux
IEH	Institute for Environment and Health
NF	nanofiltration
NSAIDs	non-steroidal anti-inflammatories
OECD	Organization for Economic Cooperation and Development
PPCPs	pharmaceuticals and personal care products
RO	reverse osmosis
STWs	sewage treatment works
T	temperature
Tr	reaction time
UBA	German Federal Environmental Agency
WHO	World Health Organization

the list of EDCs includes pesticides (e.g. DDT, vinclozolin, TBT, atrazine), persistent organochlorines and organohalogens (e.g. PCBs, dioxins, furans, brominated fire retardants), alkyl phenols (e.g. nonylphenol and octylphenol), heavy metals (e.g. cadmium, lead, mercury), phytoestrogens (e.g. isoflavoids, lignans, β -sitosterol) and synthetic and natural hormones (e.g. 17β -estradiol, 17α -ethinylestradiol). A more complete list with approximately 560 substances can be found in the Annex 1 of the CEC report [4] of the Commission of the European Communities.

The effects associated with the presence of EDC in the environment are: (1) reduction in the breakage of eggs of birds, fishes and turtles, (2) feminization of male fish, (3) some problems in the reproductive system in fishes, reptiles, birds and mammals, and (4) changes in the immunologic system of marine mammals. In some cases, these effects can lead to declines in populations. The effects of EDC's in human beings reported so far have been (1) reduction of the amount of sperm, (2) increase of the incidence of breast, (3) of testicle and prostate cancers, and (4) the endometriosis.

Some PPCPs are suspicious of causing harmful effects to the endocrine system, being also classified within EDCs. Another effect caused by pharmaceutical compounds in the environment that has also been discussed in the literature is the development of bacteria resistance to antibiotics [5,6].

PPCPs are a group of compounds which include pharmaceutical drugs, ingredients in cosmetics, food supplements and other personal care products, as well as their respective metabolites and transformation products [7]. PPCPs are continuously introduced into the environment and are prevalent at small concentrations [8], which can affect water quality and potentially impact drinking water supplies, ecosystem and human health [9–11]. Typical sources of PPCPs are sewage effluents and hospital and animal waste. Effluents from sewage treatment plants contain a variety of PPCPs, which are not completely removed in sewage treatment plants [12–14] and are released into receiving water systems. Hence, it is necessary to treat the effluents containing pharmaceuticals adequately before discharging them or treat intake waters for drinking water treatment plants. Some of the PPCPs that have been reported in the aquatic environment are: analgesics and anti-inflammatory drugs, antibiotics/bacteriostatics (antibacterial drugs), antiepileptic drugs, beta-blockers, blood lipid regulators, cytostatic drugs, oral contraceptives, antiseptics, musk fragrances and sun screen agents and others [7,15,16]. Table 2 shows a list containing some chemical classified as PPCPs.

The effect of these micropollutants in the environment does not only depend on its concentration in the environment, but also on other factors, such as lipofility increases or persistence, bioaccumulation, exposition time and mechanisms of biotransformation and elimination. Some substances in the environment suffer biotransformations, giving metabolites or by-products more harmful than the original compounds.

EDCs and PPCPs have been detected in wastewater and in treated wastewater effluents at concentrations ranging from 1.0 ng L^{-1} to $1.0 \mu\text{g L}^{-1}$, possibly due to incomplete removal during sewage treatment [14]. The reuse of wastewater on agricultural lands may transfer these compounds to the soil environment, and due to the high polarity of these compounds, there could be leaches into groundwater. Fig. 1 presents possible routes of exposition to some emerging pollutants.

The potential effects of these “emergent” contaminants in water are still uncertain and they require further investigation. Nowadays, different government and non-government organizations as the European Union (EU), the North American Environmental Protection Agency (EPA), the World Health Organization (WHO), or the International Program of Chemical Safety (IPCS) are considering this problem and setting up directives and legal frameworks to protect and improve the quality of fresh water resources. Table 3 gives some relevant information found by government and non-government organizations related to EDCs and PPCPs.

As it can be observed in Table 3, the EU and the USA are very sensible to these new emergent pollutants, which have the potential to create serious problems in the near future.

Table 1
List of some chemical classified as EDC

EDC class	Compound detected	Use/origin
Phthalates	Butylbenzylphthalate, di-(2-ethylhexyl)phthalate and di- <i>n</i> -butylphthalate	They are found in detergents, resins, some additives and monomers used in the production of plastics
Pesticides	DDT, DDE, deltamethrin, carbofuran, atrazine, lindane, vinclozolin, carbendazim and tributyltin	Extensively used in agriculture. Insecticides, herbicides and fungicides are included in this class
Organotin compounds	Tributyltin and triphenyltin	Compounds used in antifouling paints on ships
Alkylphenols (surfactants)	Nonylphenol, nonylphenol etoxylate, octylphenol, octylphenol etoxylate	They are used during the production of phenol resins, as plastic additives, emulsifiers, in agricultural and industrial applications
Dioxins and furans	Dibenzo- <i>p</i> -dioxin, 2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin and 2,3,7,8-tetrachlorodibenzofuran	They can be produced during the incineration of chlorinated aromatic compounds, paper and in the production of PVC plastic
Bisphenols	Bisphenol A	Bisphenol A is used in the manufacture of polymers (polycarbonates and epoxy resins), flame retardants and rubber chemicals
Parabens	Methyl, ethyl, propyl and butylparabens	Compounds used as preservatives in most cosmetics, personal care products
Polychlorinated biphenyls (PCBs)	2,2',4,4'-Tetrabrominated diphenyl ether, 2,5-dichloro-4, hydroxybiphenyl	PCBs have been used as coolants and lubricants in transformers, capacitors, and other electrical equipment. Although they are no longer being used, they are present in some old installation
Polycyclic aromatic hydrocarbons	Fluorene, phenanthrene, fluoranthene, anthracene, pyrene, and naphthalene	Compounds generated during incomplete combustion processes of coal, oil, and wood
Brominated flame retardants	Hexabromocyclododecane, poly-brominated diphenyl ethers and tetrabromobisphenol A	Compounds used in many products including furniture, textiles, electronic equipment
Pharmaceuticals (synthetic steroids)	Diethylstilbestrol and 17 α -ethinylestradiol	Pharmaceuticals mainly consists of oral contraceptives as well as steroids used for substitution therapy during menopause
Phytoestrogens	Daidzen and genistein, matairesol, enterodiol and enterolactone	Natural substances found in many food plants such as grains, cereals, vegetables, fruits and others
Natural hormones	Estrone, 17 β -estradiol	Estrogens naturally and daily excreted in the human urine and animals
Heavy metals	Cadmium, mercury and lead	Industrial mining and metallurgy

2. Potential treatment technologies in removing or reducing EDCs and PPCPs

In general, the techniques available for treating organic pollutants in aqueous solution are very diverse and frequently one

or more treatment techniques are required to degrade these compounds [34]. Depending on the target compound, different destructive methods that allow the efficient elimination of the pollutant from an aqueous form can be chosen, for example: chemical oxidation, incineration or degradation. On the other

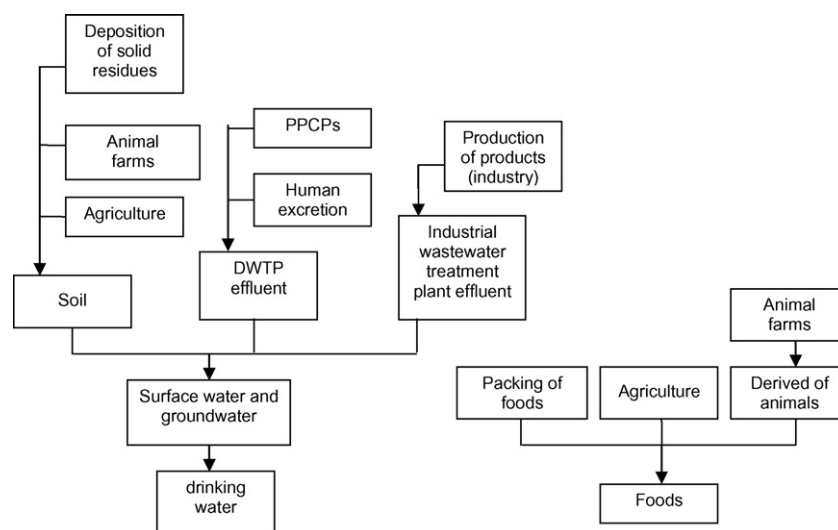


Fig. 1. Possible routes of exposition for some emergent pollutants.

Table 2
List of some chemical classified as PPCPs

PPCP class	Compound detected	Use/origin
Analgesics/non-steroidal anti-inflammatories (NSAIDs)	Acetaminophen (analgesic), diclofenac, ibuprofen, ketoprofen, naproxen, phenazone, indomethacine	NSAIDs are the most used and abused drugs in the world today. All NSAIDs have analgesic, antipyretic and anti-inflammatory effect
Antibiotics/antimicrobials	Sulfonamides, fluoroquinolones, trimetoprim, chlortetracycline, erythromycin, lincomycin, oxytetracycline, tetracycline, roxithromycin, tylosin	Antibiotics/antimicrobials are vital medicines for the treatment of bacterial infections in both humans and animals
Antiepileptics	Carbamazepine	Antiepileptics are commonly used in medicine to stop, prevent, or control seizures (convulsions, partial seizures, generalized tonic-clonic seizures, etc.)
Antihypertensives	Bisoprolol, metoprolol, propranolol	Antihypertensives are used to reduce the blood pressure in the arteries. It is difficult to prevent the hypertension, because a high blood pressure does not usually give signs or symptoms
Antineoplastics	Cyclophosphamide, ifosfamide	Antineoplastics are commonly used in the treatment of various solid tumors, lymphomas, leukemias and in some autoimmune disorders such as rheumatoid arthritis
Antiseptics	Triclosan	Antiseptics are chemical agents that slow or stop the growth of microorganisms (germs) on external surfaces of the body and help prevent infections. Antiseptics should be distinguished from antibiotics that destroy microorganisms inside the body, and from disinfectants, which destroy microorganisms found on inanimate (non-living) objects
Contraceptives	7 α -Ethinylestradiol	Oral contraceptives are chemicals taken by mouth to inhibit normal fertility by acting on the hormonal system
Sympathomimetics (bronchodilators)	Albuterol	Bronchodilators are medicines that help open the bronchial tubes (airways) of the lungs, allowing more air to flow through them
Lipid regulators	Clofibrate, bezafibrate	Lipid regulators may be used to lower cholesterol and triglyceride (fat-like substances) levels in the blood
Musks fragrances (synthetic)	Nitromusks, galaxoline, tonalide, polycyclic musks, reduced metabolites of nitromusks	Synthetic musk fragrances are commonly used in perfumery
Anti-anxiety/hypnotic agents	Diazepam	Anti-anxiety/hypnotic agents are used to relieve anxiety, nervousness, and tension associated with anxiety disorders
Sun screen agents	Benzophenone, methylbenzylidene camphor, octylmethoxycinnamate	Sun screen agents provide the protection against the harmful effects of the ultraviolet radiation coming from the sun
X-ray contrast agents	Diatrizoate, iopamidol, iopromide, iomepol	Radiocontrast agents (or simply contrast agents) are compounds used to improve the visibility of internal bodily structures in an X-ray image

hand, the non-destructive methods that allow the recuperation of the pollutant are: liquid extraction, absorption and membrane processes. The application of either of them will depend on the concentration of the effluent and the properties of the compounds in the effluent.

Basically, the choice of either one of these methods depends on the cost of the process and other factors such as concentrations and volume flows of the effluent to be treated.

Activated sludge biological treatment is recognized as the cheapest available technology to remove and degrade contaminants. But in the case of micropollutants, these substances are not completely removed by activated sludge sewage treatment [35]. Besides, a part of these micropollutants can be adsorbed in the biological sludge [13].

The removal of some pharmaceutical drugs during water treatment at laboratory and pilot plant scales were studied by different researchers. As a conclusion, in some cases it was possible to remove 90% of the antibiotics [36,37] using conventional water treatment operations such as filtration, activated carbon adsorption, reverse osmosis, chlorine or

ozone oxidation. It is possible to conclude that processes as coagulation–flocculation with aluminum or iron salts and UV-disinfection treatments did not reach good levels of contaminant removal.

Ternes et al. [38] investigated the processes of: coagulation–flocculation (with FeCl₃), activated carbon adsorption and ozonation in pilot plants and drinking water treatment plants, in the removal of other micropollutants, such as, carbamazepine, bezafibrate, clofibric acid and diclofenac. Good removal rates were reached with the processes of activated carbon adsorption and ozonation. However, in the case of the clofibric acid moderated, good removal rates were reached with ozonation processes. Once again, the coagulation–flocculation presented a low removal for micropollutants.

Removals from 60% to 99% were reached for the estrogens 17 β -estradiol and 17 α -ethinylestradiol using activated carbon [39–41].

The application of membrane processes like nanofiltration (NF) and reverse osmosis (RO) in water treatment plants are effective when removing organic micropollutant. It is possible

Table 3
Relevant information related to policies about EDCs

Year	Organization	Title of project/document	Reference
1995	UBA	Endocrinically active chemicals in the environment	[17]
1995	US EPA	Research needs for the risk assessment of health and environmental effects of endocrine disruptors: a report of the U.S. EPA-sponsored workshop	[18]
1996	US EPA	Development of a research strategy for assessing the ecological risk of endocrine disruptors	[19]
1997	US EPA	Special report on environmental endocrine disruption: an effects assessment and analysis	[20]
1998	US EPA	Endocrine disruptor screening and testing advisory committee	[21]
1998	OECD	The second meeting of the OECD validation management group (VMG) for the screening and testing of endocrine disruptors	[22]
1999	CSTEE	CSTEE opinion on human and wildlife health effects of endocrine disrupting chemicals, with emphasis on wildlife and on ecotoxicology test methods	[23]
1999	EU	A range of substances suspected of interfering with the hormone systems of humans and wildlife	[24]
2001	EU	On the implementation of the community strategy for endocrine disruptors—a range of substances suspected of interfering with the hormone systems of human and wildlife	[4]
2002	EU	Study on the scientific evaluation of 12 substances in the context of endocrine disrupter priority list of actions	[25]
2002	EU	COMPREHEND: Community program of research on endocrine disrupters and environmental hormones	[26]
2002	OECD	Appraisal of test methods for sex hormone disrupting chemicals	[27]
2002	WHO	Global assessment of the state of the science of endocrine disruptors	[28]
2003	IEH	Information exchange and international co-ordination on endocrine disruptors	[29]
2003	EU	ERAVMIS: environmental risk assessment of veterinary medicines in slurry	[30]
2003	EU	REMPHARMAWATER: ecotoxicological assessments and removal technologies for pharmaceuticals in wastewater	[31]
2004	EU	POSEIDON: assessment of technologies for the removal of pharmaceuticals and personal care products in sewage and drinking water facilities to improve the indirect potable water reuse	[32]
2004	EU	Commission staff working document: on implementation of the community strategy for endocrine disruptors—a range of substances suspected of interfering with the hormone systems of humans and wildlife COM (1999) 706	[33]

to find studies in the literature with 95% removals of EDCs and PPCPs [42,43]. Oxidation by chlorine and biological filters, coupled with MnO₂, gave good results in the removal of some EDCs [40,44]. Moreover, Snyder et al. [45] did an exhaustive study on pharmaceuticals, personal care products and endocrine disrupters found in water and the different operations tested for their removal.

2.1. Removal of EDCs and PPCPs by AOPs and ozonation

There is a group of chemical-oxidative processes called advanced oxidation processes (AOP), characterized by the generation of hydroxyl radicals. Besides fluorine, the hydroxyl radical is the strongest known oxidant. Therefore, it is possible for the hydroxyl radical to oxidize and mineralize almost every organic molecule into CO₂ and inorganic ions. Rate constants for most reactions involving hydroxyl radicals in aqueous solution are usually in the order of 10⁶ to 10⁹ mol L⁻¹ s⁻¹ [46,47]. Different techniques may be used to generate hydroxyl radicals. Some of these techniques are characterized for the use of UV radiation and the presence of oxidants as hydrogen peroxide and ozone (light oxidation processes). Nevertheless, it is possible to generation hydroxyl radicals without radiation. In fact, the most common technique used at industrial level is the Fenton process, which only uses iron salt and hydrogen peroxide at acidic conditions [48].

Tables 4 and 5 show the results of different AOPs used to remove EDCs and PPCPs from aqueous samples and sewage effluents. Most of these studies were carried out at laboratory scale, but there are some interesting ones performed in water treatment plants. Table 4 presents the list of com-

pounds removed by using dark oxidation processes whereas Table 5 corresponds to the processes which used light (ultraviolet radiation).

According to the information supplied in Table 4, ozonation is the dark oxidation method most used in the removal of these new emergent pollutants. Approximately 90% of the dark oxidation treatments found in the scientific literature corresponds to ozonation. The pollutants removals were obtained by using ozone dose from 0.1 to 30 mg L⁻¹. Removals higher than 90% were reached for several compounds, such as, pesticides, anti-inflammatories, antiepileptics, antibiotics and natural and synthetic estrogens. However, some substances seem to be a little more recalcitrant to the oxidation (clofibric acid and X-ray contrast agents). Fenton treatment has been used successfully as a dark oxidation method to remove herbicides and antibiotics. Even though that Fenton is an important oxidation treatment for industrial wastewaters [48], only few papers targeting the removal of EDCs and PPCPs are found in the literature. Nevertheless, in all dark treatments reviewed the TOC removal was not so high, in other words, low mineralization of micropollutants were reached.

UV/H₂O₂ and titanium dioxide photocatalysis are the light oxidation processes most used to destroy EDCs and PPCPs. Removals higher than 98% were obtained by using TiO₂ photocatalysis, estrogens (17β-estradiol, estrone and 17α-ethinylestradiol), bisphenols and antiepileptics. In order to achieve high removals, large irradiation times were required compared with dark ozonation processes. As in the ozonation, the TOC removals were small. In the literature, UV lamps are used as source of radiation and only one of the manuscripts found uses simulated solar radiation (from a Xe lamp). The range of H₂O₂ concentrations used went from 0.1 to 1 mol L⁻¹). Estra-

Table 4
Dark oxidation processes

Year	Compound	Type of water	Treatment	Operating conditions	Results and comments	References
2000	Pesticides (atrazine and some phenylurea herbicides)	Groundwater	O ₃ /H ₂ O ₂ Fenton (Fe ²⁺ /H ₂ O ₂) Ozonation	pH 7.8 ratio H ₂ O ₂ /O ₃ = 3.7 g g ⁻¹ ; C _{H₂O₂} = 8.8 mg L ⁻¹ pH 5.5; C _{H₂O₂} = 10 mg L ⁻¹ ; C _{Fe²⁺} = 5.1 mg L ⁻¹ C _{O₃} = 1.0 mg L ⁻¹ ; Tr = 10 min; C ₀ = 2 µg L ⁻¹ , distilled water C _{O₃} = 1.0 mg L ⁻¹ ; Tr = 10 min; C ₀ = 2 µg L ⁻¹ , distilled water C _{O₃} = 1.0 mg L ⁻¹ ; Tr = 10 min; C ₀ = 2 µg L ⁻¹ , drinking water C _{O₃} = 3.7 mg L ⁻¹ ; Tr = 10 min; C ₀ = 2 µg L ⁻¹ , drinking water C _{O₃} = 5.0 mg L ⁻¹ ; Tr = 10 min; C ₀ = 2 µg L ⁻¹ , drinking water	80% removal of atrazine and some phenylurea herbicides; 99% removal of atrazine 75% removal of atrazine and 94% of some phenylurea herbicides 8% of clofibric acid, 12% of ibuprofen and 97% of diclorfenac were removed 50% of clofibric acid, 50% of ibuprofen and 100% of diclorfenac were removed 10% of clofibric acid, 30% of ibuprofen and 100% of diclorfenac were removed 90% of clofibric acid, 90% of ibuprofen and 100% of diclorfenac were removed 97.9% of clofibric acid, 99.4% of ibuprofen and 100% of diclorfenac were removed	Ijeplaar et al. [49]
2000	Clofibric acid, ibuprofen and diclofenac	Distilled and drinking water	O ₃ /H ₂ O ₂ molar ratio (O ₃ /H ₂ O ₂) = 2:1	Ratio O ₃ /CBZ = 10; C ₀ = 0.8 mg L ⁻¹ ; C _{O₃} = 1.0 mg L ⁻¹ ; Tr = 10 min Ratio O ₃ /CBZ = 10; C ₀ = 118 mg L ⁻¹ ; Tr = 10–60 min C _{O₃} = 0.3 mg L ⁻¹ ; Tr = 0–1.5 min; pH 7.5	Complete removal of carbamazepine in natural water was reached. After 60 min of treatment a little TOC removal was observed	Andreozzi et al. [51]
2002	Carbamazepine	Aqueous solution	Ozonation	C ₀ = 1 µg L ⁻¹ ; C _{O₃} = 0.5–3.0 mg L ⁻¹ ; Tr = 20 min	95% removal of all compounds in natural water	Adams, et al. [36]
2002	Antibiotics (carbadox, sulfachlorpyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfathiazol, trimethoprim)	Deionized and river water	Ozonation		97% removal of all compounds in natural water	Adams, et al. [36]
2002	Carbamazepine, bezafibrate, diclofenac and clofibric acid	Distilled and drinking water	Ozonation	C ₀ = 1 µg L ⁻¹ ; C _{O₃} = 0.5–3.0 mg L ⁻¹ ; Tr = 20 min	97% of carbamazepine and diclofenac were eliminated with ozone dose of 0.5 mg L ⁻¹ . Bezafibrate was 50% removed with ozone dose of 1.0–1.5 mg L ⁻¹ and 90% was removed with ozone dose 3.0 mg L ⁻¹ . Only 10–15% removal of clofibric acid with 0.5 mg L ⁻¹ ozone dose. At higher ozone dose (2.5–3.0 mg L ⁻¹) 40% of chlofibric acid was removed	Ternes et al. [38]
2003	Paracetamol	Aqueous solution	Ozonation	pH 2.0 and 7.0; C ₀ = 5.0 mmol L ⁻¹ ; T = 25 °C	Complete removal of paracetamol with 30% mineralization. Oxalic, glyoxalic, cetomalonic and formic acids and hydroquinone were identified as intermediates	Andreozzi et al. [52]
2003	Chlofibric acid	Aqueous solution	Ozonation	Tr = 60 min; pH 2.0–6.0; C ₀ = 1.0–1.5 mmol L ⁻¹ ; C _{O₃} aqueous = 1.0 × 10 ⁻⁵ mol L ⁻¹	100% removal of clofibric acid was reached in 20 min with 34% mineralization. 49% mineralization was reached in 60 min. No halogenocompounds were detected in the oxidation products	Andreozzi et al. [53]
2003	Bezafibrate, carbamazepine, diazepam, diclofenac, 17α-ethinylestradiol, ibuprofen, iopromide, sulfametoxazol and roxithromycin	Milli Q, river and lake water	Ozonation	C _{O₃} = 0.1; 0.2; 0.5; 1.0 and 2.0 mg L ⁻¹ ; C ₀ = 0.5 µmol L ⁻¹ ; natural water properties: pH 7.2–7.9; COD = 0.8–3.7 mg L ⁻¹ ; alcalinity = 0.7–5.8 mol L ⁻¹ HCO ₃ ⁻	Ozone doses ranging from 0.2 up 0.5 mg L ⁻¹ were observed with 97% removal of all compounds. Removal of bezafibrate was lower	Huber et al. [54]

2003	Iodinated X-ray contrast media antibiotics, betablockers, antiphlogistics, lipid regulator metabolites, antiepileptics and estrogens	DWTP effluent	Ozonation	$C_{O_3} = 5, 10, 15 \text{ mg L}^{-1}$; effluent properties: pH 7.2; DOC = 23 mg L^{-1} ; COD = 30 mg L^{-1} ; SST = 4.5 mg L^{-1}	Ozone doses ranging from 5 up to 15 mg L^{-1} were necessary for complete removal of these compounds. The only exceptions were iodinated X-ray contrast media which were removed 13–89% with ozone doses from 10 to 15 mg L^{-1} , respectively	Ternes et al. [55]
2004	Estrogens (17 β -estradiol and 17 α -ethinylestradiol) and bisphenol (bisphenol A)	Distilled water	Ozonation	$C_0 = 100 \text{ nmol L}^{-1}$; $T = 20^\circ \text{C}$; contact time = 1–120 min; $C_{O_3} = 1.5 \text{ mg L}^{-1}$	100% removal of bisphenol A, 17 β -estradiol and 17 α -ethinylestradiol. A reduction of estrogenic activity was reached	Alum et al. [44]
2004	Diclofenac	Distilled water	Ozonation	pH 5.0; 5.5 and 6.0; scavenger = <i>tert</i> -butyl alcohol; $C_0 = 0.1 \text{ mmol L}^{-1}$; C_{O_3} aqueous = 0.1 mmol L^{-1}	100% of chlorine release was observed and 32% mineralization	Vogna et al. [56]
2004	Natural estrogen (17 β -estradiol)	Distilled water	Ozonation	$C_0 = 5.2 \text{ } \mu\text{mol L}^{-1}$; $T = 20^\circ \text{C}$; contact time 30 min; $C_{O_3} = 5.0 - 15 \text{ mg L}^{-1}$; pH 6.0; experiments with and without fluvic acid	99% removal of 17 β -estradiol with ozone dose of 5 mg L^{-1} in 15 min or ozone dose of 15 mg L^{-1} in 4 min. It was observed a reduction of estrogenic activity	Kim et al. [57]
2004	Synthetic estrogen (17 α -ethinylestradiol)	Milli Q purified water	Ozonation	$C_0 = 1$ to $10 \text{ } \mu\text{mol L}^{-1}$; pH 8; $C_{O_3} = 5$ to $24 \text{ } \mu\text{mol L}^{-1}$; $C_{O_3} = 50$ to $100 \text{ } \mu\text{mol L}^{-1}$	Oxidation products formed during the ozonation of 17 α -ethinylestradiol were identified. Ozone doses ranging from 0.5 up to 10 mg L^{-1} removed estrogenicity. Authors suggested that estrogenicity reduction can be attributed to the cleavage of the phenolic moiety	Huber et al. [58]
2005	Antibiotic (amoxicillin)	Aqueous solution	Ozonation	$C_0 = 0.5 \text{ mmol L}^{-1}$; $C_{O_3} = 0.16 \text{ mmol L}^{-1}$; pH 2.5–5.0	Low mineralization and some by-products were identified	Andreozzi et al. [59]
2005	Natural estrogen (17 β -estradiol)	Milli Q and distilled water	Ozonation	$C_0 = 10$ and $50 \text{ } \mu\text{g L}^{-1}$; pH 3.7 and 11; $C_{O_3} = 0.5$ to 30 mg L^{-1}	The results show that ozonation was able to promote extensive degradation of 17 β -estradiol and to reduce its estrogenic activity. The results showed that in pH 7 and 11 the estrogenic activity was not completely removed, even with an increase of the dosage of ozone	Bila et al. [60]
2005	Natural estrogen (17 β -estradiol) and bisphenol (bisphenol A)	Aqueous solution	Ozonation	$C_0 = 0.10 \text{ mmol L}^{-1}$; $C_{O_3} = 7.516 \text{ } \mu\text{mol L}^{-1}$	The reaction between bisphenol A and ozone is slower than the reaction between 17 β -estradiol and ozone	Irmak et al. [61]
2006	Pesticide (atrazine) pharmaceuticals (carbamazepine)	Drinking water	Ozonation	pH 7.5; $C_{O_3} = 1.52.0 \text{ mg L}^{-1}$	High efficiency in removing micropollutants using ozonation after filtration and coagulation/flocculation	Hua et al. [62]
2006	Antibiotic (clarithromycin)	Milli Q water	Ozonation	$C_0 = 0.1 \text{ mmol L}^{-1}$; $C_{O_3} = 10 \text{ } \mu\text{mol L}^{-1}$; $T = 20^\circ \text{C}$	Biological activity of clarithromycin was reduced after ozonation	Lange et al. [63]
2006	Pesticides (alachlor, atrazine, chlorfenvinphos, isobroturum, diuron)	Distilled water	Ozonation	$C_{O_3} = 26.8 \text{ g m}^{-3}$; $C_0 = 16-20 \text{ mg L}^{-1}$	Large amounts of ozone were spent to remove pesticides. Complete removal of TOC was hard to achieve	Maldonado et al. [64]
2006	Antibiotic (metronidazol)	Deionized water	Fenton	$C_0 = 6.0 \text{ } \mu\text{mol L}^{-1}$	Fenton was less efficient than photo-Fenton	Shemer et al. [65]
2007	Benzafibrate (lipid regulator)	Distilled water	Ozonation	$C_{O_3} = 1 \text{ } \mu\text{mol L}^{-1}$; $C_0 = 0.2-0. \text{ } \mu\text{mol L}^{-1}$; pH 6 to 8	The complete BZF abatement is achieved. However, only a small part of the substrate is mineralised	Dantas et al. [66]
2007	Pharmaceutical and personal care products	Groundwater	Ozonation	$C_0 = 4$ and $400 \text{ } \mu\text{mol L}^{-1}$; $C_{O_3} = 20 \text{ mg L}^{-1}$	No significant influence of ozone pre-treatment was observed on PPCPs elimination except for carbamazepine	Carballa et al. [67]
2007	Ibuprofen, bezafibrate, amoxicillin, sulfamethoxazole	Pure water	Ozonation	$C_0 = 10 \text{ } \mu\text{mol L}^{-1}$	In the ozone-Membrane Filtration hybrid experiments, the pre-ozonation was able to reduce the membrane fouling	Soo Oh et al. [68]

Table 5
Light oxidation processes

Year	Compound	Type of Water	Treatment	Operating conditions	Results and comments	References
2000	17 β -Estradiol	Aqueous solution	Photocatalysis	150 W lamp; $C_0 = 0.05\text{--}3 \mu\text{mol L}^{-1}$; membrane TiO ₂ of 1.5 mg cm^{-2}	50% of 17 β -estradiol was removed in 40 min and 98% removal in 3.5 h	Coleman et al. [69]
2001	Bisphenol A	Doubly distilled water	Photocatalysis	200 W Hg–Xe lamp; $C_0 = 175 \mu\text{mol L}^{-1}$; $I = 10 \text{ mW cm}^{-2}$; TiO ₂ in suspension	100% mineralization of bisphenol A was mineralization in 20 h. Estrogenic activity reduced to 10% after 6 h of treatment	Ohko et al. [70]
2002	Antibiotics (carbadox, sulfachlorpyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfathiazol, trimethoprim)	Distilled, deionized water and river water	UV	Low pressure lamp (254 nm); $C_0 = 20$ and 50 mg L^{-1} ; $T = 20 \text{ }^\circ\text{C}$; pH 7.5; Tr = 30 min	Normal UV dose (30 mJ cm^{-2}) used in water treatment plants were not enough to remove antibiotics. By using UV dose of 3.0 J cm^{-2} , antibiotic removals between 50% and 80% were reached	Adams et al. [36]
2002	17 β -Estradiol and bisphenol A	Distilled water	Photocatalysis	Black blue lamp (15 W); $C_0 = 90 \mu\text{g L}^{-1}$; $I = 0.24 \text{ mW cm}^{-2}$; TiO ₂ immobilized in PTFE	98% removal in 1 h of treatment	Nakashima et al. [71]
2002	17 β -Estradiol	Aqueous solution	Photocatalysis	UV lamp (200 W); $C_{\text{TiO}_2} = 1 \text{ g L}^{-1}$; $C_0 = 1 \mu\text{mol L}^{-1}$; $I = 6 \text{ mW cm}^{-2}$; TiO ₂ in suspension	More than 99% removal of 17 β -estradiol in 30 min. Treatment of 3 h was necessary to complete mineralization. No estrogenic activity of the products formed was observed	Ohko et al. [72]
2003	Paracetamol	Bi-distilled water	H ₂ O ₂ /UV	Low pressure lamp (17 W, 254 nm); $C_{\text{H}_2\text{O}_2} = 5$ and 20 mmol L^{-1} ; pH 2.0–7.0	Complete removal of paracetamol with mineralization between 21% and 40% by using H ₂ O ₂ concentrations of 5.0 and 20 mmol L ⁻¹ , respectively. Intermediate compounds identified: hydroquinone, 2 hydroxi-4- <i>N</i> -acetyl-aminophenol and dicarboxylic acids	Andreozzi et al. [52]
2003	Clofibric acid	Aqueous solution	H ₂ O ₂ /UV	Low pressure lamp (17 W, 254 nm); $C_0 = 1.0 \text{ mmol L}^{-1}$; $C_{\text{H}_2\text{O}_2} = 1.0 \text{ mol L}^{-1}$; pH 5; Tr = 60 min	Almost complete removal of clofibric acid in 60 min with small mineralization	Andreozzi et al. [53]
2003	Estrone and 17 β -estradiol	Distilled water and DWTP effluent	Photocatalysis	Black blue lamp (15 W); $C_0 = 250 \mu\text{g L}^{-1}$; $I = 1.2 \text{ mW cm}^{-2}$; TiO ₂ immobilized in PTFE	17 β -Estradiol and estrone were fastly removed. 90% removal of estrone reached in DWTP effluent	Nakashima et al. [73]
2004	17 β -Estradiol, estrone and 17 α -ethinylestradiol	Sterile double distilled water	Photolysis and photocatalysis	High pressure Hg lamp (152 W); $C_0 = 10 \mu\text{g L}^{-1}$; TiO ₂ immobilized; UVA lamp (photolysis)	Very fast removal of estrogenic activity of the three compounds tested by using photocatalysis. 50% of estrogenic activity was removed in 10 min. Removals of 100% were reached in 1 h of treatment. Photolysis needs more time to remove estrogenic activity	Coleman et al. [74]
2004	Carbamazepine	Doubly distilled water	H ₂ O ₂ /UV	Low pressure lamp (254 nm); $C_0 = 20 \mu\text{mol L}^{-1}$; $C_{\text{H}_2\text{O}_2} = 5.0 \text{ mmol L}^{-1}$; pH 5; Tr = 4 min	100% removal of carbamazepina in 4 min of treatment with a 35% removal of TOC. Intermediates formed in the oxidation were more toxic than the original pharmaceutical	Vogna et al. [75]

2004	Diclofenac	Doubly distilled water	H ₂ O ₂ /UV	Low pressure lamp (17 W, 254 nm); $I_0 = 2.7 \mu\text{Einstein s}^{-1}$; $C_0 = 1.0 \mu\text{mol L}^{-1}$; $C_{\text{H}_2\text{O}_2} = 0.1 \text{ or } 1.0 \text{ mol L}^{-1}$; pH 7.0	100% removal of diclofenac with a complete release of chlorine by using H ₂ O ₂ /UV. Almost 40% of chlorine formed chlorate ions	Vogna et al. [56]
2004	Estrone, 17 β -estradiol	Double distilled water	UV (photolysis)	UV-light (30 W); UV-vis-light (125 W); $C_0 = 3\text{--}10 \text{ mg L}^{-1}$	Two estrogens in aqueous solutions undergo fast direct photolysis under irradiation with UV disinfection lamp. High-pressure mercury lamp can also induce the photolysis of estrone. Both the estrogens photolyzed undergo the breakage and oxidation of benzene rings producing compounds containing carbonyl groups	Liu and Liu [76]
2004	Bisphenol A, 17 β -estradiol and 17 α -ethinylestradiol	Deionized water, model natural drinking water and river water	UV/H ₂ O ₂	Medium pressure and low pressure UV lamp; $C_{\text{H}_2\text{O}_2} = 200 \text{ mg L}^{-1}$; pH 6.0–8.0	Addition of H ₂ O ₂ gives greater removals of contaminant when compared to no H ₂ O ₂ addition	Rosenfeldt and Linden [77]
2005	17 β -estradiol, 17 α -ethinylestradiol and estriol	Milli Q water	Photolysis and photocatalysis	TiO ₂ immobilized high pressure Hg lamp (250 W); pH 3.5–4.0; $C_0 = 3 \mu\text{mol L}^{-1}$	Complete removal of these compounds was reached. Photocatalysis was more efficient than photolysis	Coleman et al. [78]
2005	Clofibric acid, carbamazepine, iomeprol	Ultrapure water	Photocatalysis	TiO ₂ in suspension; solar simulator (1 kW Xe lamp)	Efficient removal degree was reached by using photocatalysis	Doll and Frimmel [79]
2005	Estrone, 17 β -estradiol, 17 α -ethinylestradiol and diethylstilbestrol	Aqueous solution	Photo-Fenton	250 W metal halide lamp; $C_0 = 5 \text{ mg L}^{-1}$; pH 3.0–8.0	Some difficulties in removing estrone were observed. Efficiency depends on initial pH and Fe ³⁺ and H ₂ O ₂ concentrations. Compounds arranged according to ease of degradation: diethylstilbestrol > 17 β -estradiol > 17 α -ethinylestradiol > estrone	Feng et al. [80]
2005	Antibiotic (amoxiciline)	Aqueous solution	UV/H ₂ O ₂	Low pressure lamp (254 W); $C_0 = 0.5 \text{ mmol L}^{-1}$	The kinetic constant for the direct attack depends strongly in the pH of the solutions. UV/H ₂ O ₂ was used to evaluate the constant for the OH radical attack to the amoxicillin molecule at pH 5.5. Kinetic constant obtained $K_{\text{OH,AM}} = 3.93 \text{ nmol L}^{-1} \text{ s}^{-1}$	Andreozzi et al. [59]
2006	Antibiotic (metronidazol)	Deionized water	UV photo-Fenton UV/H ₂ O ₂	Low pressure lamp; UV = 0–600 mJ cm ⁻² ; $C_{\text{H}_2\text{O}_2} = 25\text{--}50 \text{ mg L}^{-1}$; $C_0 = 6 \mu\text{mol L}^{-1}$; pH (UV) = 6 pH (photo-Fenton) = 3.5	UV provides small degradation compared to UV/H ₂ O ₂ . Photo-Fenton gives 20% higher removal than Fenton	Shemer et al. [65]
2006	Bisphenol A	Milli Q deionized water	UV UV/H ₂ O ₂	Low pressure lamp (15 W, 254 nm); $C_0 = 60 \mu\text{mol L}^{-1}$; $C_{\text{H}_2\text{O}_2} = 0 \text{ to } 50 \text{ mg L}^{-1}$; pH 5.3–4.3	UV was not enough to degrade bisphenol A. Experiments with UV/H ₂ O ₂ give a better removal of estrogenic activity	Chen et al. [81]
2007	Herbicide of metsulfuron-methyl (MM)	Distilled water	Photocatalysis	TiO ₂ was dosed at a rate of 1.5 g L^{-1} ; $C_0 = 10 \text{ mg L}^{-1}$	The system had a high removal rate of over 90%	Areerachakul et al. [82]
2007	Sulfonylurea herbicide	Milli Q water	Photocalatalysis	Light source HPK 125 W Philips (365 nm); $C_0 = 25, 15, 10 \text{ and } 5 \text{ mg L}^{-1}$	The degradation rate was strongly affected by the TiO ₂ amount and the light flux. More than 20 intermediates were unambiguously identified	Sleiman et al. [83]

diol and bisphenol A are the compounds whose removals by oxidation treatment have been more studied.

Recently, studies on the estrogenic activity removal of some pollutants (17 β -estradiol, 17 α -ethinylestradiol and bisphenol A) were carried out. It was observed that oxidation processes, such as ozonation and photocatalysis, are able to remove the estrogenic activity significantly. However, in some cases, a residual activity still remains after the treatment.

Investigations about treatment processes for EDC and PPCs removal are relatively recent. These studies have been published since 2000. On the other hand, the studies of identification of these compounds in the environment and their effects have already been reported for a long time in the literature. The effects in the endocrine system of laboratory animals by estrogenic substances were evidenced for the first time around 1923 [84,85].

Works on the removal of EDCs and PPCs were carried out at laboratory scale to obtain information on their removal kinetics and mainly on the formation and degradation of by-products. Nowadays the research is focusing the removal of the biological activity of micropollutants, and also to collect information about the capability of conventional water and wastewater treatment processes to remove these pollutants and their biological activity. Therefore, this current approach is of paramount importance, in order to improve the performance of the DWTPs, which should consider not only the removal of the classical global parameters, but the removal of these emergent pollutants and their bioactivities.

3. Conclusions

It is essential to know how effective are the processes used today for the removal of these micropollutants and their biological activities. This step is of paramount importance in order to improve the performance DWTPs and consider the removal of these emergent pollutants and not only the global organic matter parameters:

- Public awareness and policy attention have recently increased the studies about removal of EDCs and PPCs in water and wastewater treatment processes.
- Physical separation methods as activated carbon adsorption and membrane processes are able to remove EDCs and PPCs in water effluents.
- Advanced oxidation processes are appropriate to oxidize these compounds.
- Ozonation was the oxidation process most studied which gives good expectatives to be applied with success.
- Estrogenic activity depends on the specific oxidation treatment carried out.

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